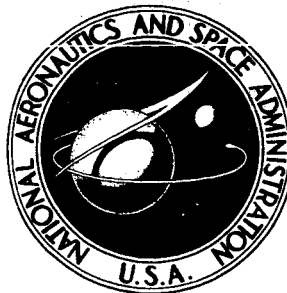


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**PREPARATION AND ROLL
COMPACTION OF TUNGSTEN-COATED
URANIUM DIOXIDE PARTICLES**

by Gordon K. Watson, Robert M. Caves, and Neal T. Saunders

Lewis Research Center

Cleveland, Ohio

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PREPARATION AND ROLL COMPACTION OF TUNGSTEN-COATED URANIUM DIOXIDE PARTICLES (U)

by Gordon K. Watson, Robert M. Caves, and Neal T. Saunders

Lewis Research Center

SUMMARY

Several methods of tungsten (W) coating uranium dioxide (UO_2) particles were investigated, and commercially produced coated particles were evaluated in the as-received condition and after testing at temperatures up to 2500°C . The results indicated that the halide-vapor deposition techniques are the most promising of those examined for producing W-coated UO_2 particles. At the current state of development, only the chloride coating process (hydrogen reduction of tungsten hexachloride) has demonstrated capability of consistently producing high-quality coatings for this application. However, a duplex-coating process, involving an initial thin coating layer from the chloride process and a thicker layer from a fluoride process (hydrogen reduction of tungsten hexafluoride), appears promising but needs further development.

A roll compaction process was developed for the consolidation of tungsten-coated UO_2 particles into dense cermet plates. In this process, the coated particles were compacted in molybdenum cans by hot rolling at 1700°C . After compaction, the molybdenum cans were removed by chemical dissolution. The resultant cermets were rolled an additional small amount at 1950°C to improve the surface finish. The results of this study showed that the roll compaction process is capable of producing fully dense W- UO_2 cermets of a variety of fuel loadings (up to 70-volume-percent UO_2) and UO_2 particle sizes (10 to $130\ \mu\text{m}$). It also was shown that the major surfaces of the composites could be clad with unfueled tungsten by roll bonding techniques.

INTRODUCTION

A powder-metallurgy - hot-rolling technique was developed in a previous investigation (ref. 1) for the fabrication of thin, refractory metal-base, dispersion-type fuel plates for use in the nuclear rocket concept under consideration at the NASA Lewis

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Research Center (ref. 2). The fuel plates, containing uranium dioxide (UO_2) particles dispersed in a tungsten (W) matrix, were made by blending tungsten and UO_2 powders, cold pressing, sintering, and hot rolling to the desired thickness. These plates were clad on the major surfaces with roll-bonded, unfueled tungsten foil. The fuel loading range of interest was from 10- to about 35-volume-percent UO_2 .

One problem with the fuel plates made from powder mixtures was the nonuniform dispersion of the UO_2 particles due to the poor blending characteristics of the coarse UO_2 and the fine tungsten powders used. In addition, UO_2 particles exposed at the unclad edges of the fuel plates were lost at high temperatures ($>2200^\circ\text{C}$) because of vaporization. Other UO_2 particles within the body of the plate also were lost by vaporization from the unclad edges due to interconnection of the UO_2 particles to the surfaces.

The use of tungsten-coated UO_2 particles for fuel elements was proposed as a method solving these problems. Because each UO_2 particle is encapsulated in tungsten, a uniform fuel distribution would be expected when the particles are consolidated into a dense body. Interconnection of the UO_2 particles also would be eliminated if the particle coatings remained intact. Therefore, methods of preparing and consolidating tungsten-coated UO_2 particles have been investigated.

Part of the study reported herein involved evaluation of tungsten-coated UO_2 particles commercially prepared by different processes. Emphasis was placed on vapor-deposition coating techniques using hydrogen reduction of either tungsten hexafluoride (WF_6) or tungsten hexachloride (WCl_6). The evaluation primarily was directed towards determining if the coated particles met the goals of high purity, full density, integrity, and good fuel retention at elevated temperatures. Some of the difficulties encountered in obtaining and evaluating coated particles are summarized along with the methods used to attain particles of the desired quality.

The second part of the study involved development of a method of consolidating the tungsten-coated UO_2 particles into dense cermets. Several methods of accomplishing this were simultaneously evaluated under NASA-sponsored programs. Two methods, hot isostatic compaction (ref. 3) and hot pneumatic impaction (ref. 4), were developed under NASA-sponsored contracted programs. These processes appear promising for producing W- UO_2 cermets in a variety of fuel element configurations. In addition, a hot roll compaction method was developed at the Lewis Research Center for producing cermets in plate configurations. Development of the roll compaction process, which involves hot rolling of tungsten-coated UO_2 particles in expendable molybdenum cans, is described in this report.

PREPARATION AND EVALUATION OF TUNGSTEN-COATED UO_2 PARTICLES

The tungsten-coated UO_2 particles initially used were coated commercially in a fluidized bed by the hydrogen reduction of tungsten hexafluoride ($\text{WF}_6 + 3\text{H}_2 \rightarrow \text{W} + 6\text{HF}$). Evaluation of the particles indicated difficulties which appeared to be associated with high residual fluorine contents or other impurities. Therefore, attempts were made by the coating vendors to improve the tungsten coating applied by the fluoride process. In addition, other coating processes were investigated. From these studies, a chloride-coating process was developed (involving hydrogen reduction of tungsten hexachloride, $\text{WCl}_6 + 3\text{H}_2 \rightarrow \text{W} + 6\text{HCl}$) as an attractive alternate. Thus, most of the effort was concentrated on improvement and evaluation of coated particles prepared by either the fluoride or the chloride processes, and the results are summarized in this section.

Preparation of Coated Particles

Fluoride-coating process. - The UO_2 substrate particles used in preparing all the coated particles discussed in this part of the report were nearly spheroidal (major- to minor-axis ratio of less than 2:1) and were 30 to 70 microns in diameter. Specifications required that they be heated in hydrogen (high fired) above 1700°C to produce a density of at least 92 percent of theoretical and an oxygen-to-uranium ratio of 2.000 ± 0.005 . A purity greater than 99.9-percent UO_2 was required with no single metallic impurity exceeding 200 ppm (parts per million by weight) and with carbon and total halides not exceeding 30 ppm each.

Typical examples of tungsten-coated UO_2 particles prepared by the fluoride process early in the study are shown in figure 1. These particles were coated with approximately a 15-micron thick layer of tungsten to produce a fuel loading of about 20-volume-percent UO_2 in each particle. Although the coatings on the particles appeared to be relatively good, chemical analysis of several batches of particles prepared using the fluoride process indicated residual fluorine contents in the range of 200 to 300 ppm.

Since it was believed that the fluoride impurities could have a detrimental effect on the high-temperature performance of tungsten-coated UO_2 particles, an upper limit of 75 ppm total halide content was established for subsequent procurement of coated particles. Several attempts were made by different vendors to improve control of the deposition parameters to minimize chemical reactions of the halides with the UO_2 or entrapment of residual fluorides in the tungsten. Improvements were reportedly made in lowering the fluorine content of coated particles to the required level by reducing the deposition rates; however, of 10 batches (supplied by 5 vendors) of fluoride-coated particles evaluated in this study, the lowest fluorine-contamination level was 112 ppm (as

indicated in table I). Thus, work on direct coating of UO_2 particles by the fluoride process was discontinued.

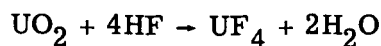
Alternate coating processes. - Because of the problems associated with reducing the fluorine content of particles coated by the fluoride process, other particle coating processes were investigated by several organizations under either private or NASA sponsorship. The most promising of these alternate processes involved hydrogen reduction of tungsten hexachloride, as described in the following paragraphs. Work on other coating methods is briefly summarized in appendix A.

The chloride process produced fully dense coatings with low chlorine content (3 to 40 ppm as indicated in table I). As-received particles coated by the chloride process appeared similar to those coated by the fluoride process (fig. 1), and the chemical analyses of trace elements, except for halides, iron, nickel, and chromium, were similar in particles coated by either process (see appendix B).

At the time the chloride process was being developed, the coating vendors indicated that the process was more expensive than the fluoride process primarily because the deposition rates used to coat UO_2 must be extremely slow to achieve low residual chlorine contents. Because of this cost factor, some particle vendors utilized a duplex-coating process in which a thin tungsten coating was applied to the UO_2 substrate particles by the chloride process, and then the remainder of the coating was applied by the less expensive fluoride process. The inner coating layer served to protect the UO_2 from interaction with byproducts of the fluoride reaction (as will be discussed in the following section). The duplex-coating process was partially successful in that the total halide content in some batches of particles prepared by this method was below the 75-ppm maximum halide limit established for coated particles. However, halide analyses of several batches of particles coated by the duplex-coating process indicated that the fluorine content varied from batch to batch (e.g., table I: lots 9-30-65A, 9-30-65B, and 9-30-65C). Thus, improved control of the duplex-coating process is needed.

Coating conditions. - Complete details of the processing conditions used in preparing tungsten-coated UO_2 particles by fluoride, chloride, or duplex-coating processes are not available because this information is considered proprietary by the coating vendors. However, it is known that coatings from the fluoride process are usually applied at temperatures of about 500°C while those from the chloride process are applied at about 900°C .

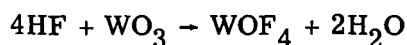
The higher deposition temperatures associated with the chloride process may account for the better control of halide impurities with this coating process. During coating with the fluoride process, the deposition reaction product HF could react with the UO_2 substrate to form uranium tetrafluoride (UF_4) by the reaction:



At the usual deposition temperatures of about 500^o C, the UF₄ product is a stable solid which could be trapped at the substrate-coating interface. Similar reaction between WCl₆ and UO₂ in the chloride-coating process would result in uranium tetrachloride (UCl₄), but this compound is in the gaseous state at the higher chloride deposition temperature. Thus, reaction products formed in the chloride process could vaporize from the coating surface during deposition. For this reason, it is desirable initially to use low deposition rates with the chloride process since more rapid deposition rates could result in entrapment of some of the UCl₄ and, thus, could increase the residual chlorine content of the particles.

The variation in fluorine content of particles coated by the duplex-coating process indicated that another mode of fluoride contamination must be occurring since the thin chloride-produced cladding should prevent reaction between the UO₂ and HF deposition products. Similar results have been reported (refs. 5 to 7) for unfueled tungsten specimens that were produced by the fluoride-vapor deposition process. In these other studies, fluorine impurity contents in the vapor-deposited tungsten ranged from near the 1-ppm limit of detection to several hundred ppm.

The observed variations in fluorine content are thought to be associated with the substrate preparation and the coating conditions used to deposit the tungsten. Any excess oxygen present in the deposition system (possibly from surface oxide contaminants on the substrates and/or oxide contaminants in the WF₆ supply source) could result in the formation of tungsten oxyfluoride (WOF₄) by reactions such as:



The WOF₄ could be entrapped in the tungsten coating with the rapid deposition rates normally used with the fluoride-coating process. Similarly, tungsten oxychlorides (WOC₄ and WO₂Cl₂) could be produced during coating with the chloride process; however, the slower deposition rates used with this process probably allow sufficient time for the contaminants to be released (or reduced) during the coating process. In addition, the higher deposition temperatures associated with the chloride process possibly allow hydrogen reduction of any substrate surface contaminants prior to coating; thus, the amount of oxychloride formed is reduced. In either process, however, closer control of oxide contaminants in the coating chambers and in the WF₆ or WCl₆ gas supplies should be exercised.

High-Temperature Evaluation of Coated Particles

The high-temperature capabilities of tungsten-coated UO_2 particles prepared by each of the three coating processes were determined by heating small (7g) samples of particles from each coating process at 2500°C for 1 hour in a hydrogen atmosphere. (Particles representative of the fluoride-, chloride-, and duplex-coating processes were taken from lots 9-30-65D, 11-12-65B, and 9-30-65B, respectively, listed in table I.) These particle samples were heated simultaneously in individual tungsten crucibles and were examined subsequently for changes in total weight, fluorine content, and microstructure. In addition to the 2500°C test, samples from the same lot of chloride-produced particles were tested at 1500°C and at 2000°C to determine the effect of lower test temperatures.

The change in weight of the particles as a result of testing was assumed to be UO_2 vaporization losses from particles with defective coatings. These losses, expressed in weight percent UO_2 , are listed in table II. In all cases, the UO_2 losses at 2500°C were less than 1 weight percent, and the differences between samples were not considered significant. The UO_2 losses from the chloride-produced particles increased with increasing temperature, probably because of the increasing vapor pressure of the UO_2 with increasing temperature. As demonstrated by the weight loss data, the particle coatings produced by any of the three processes effectively retained the fuel under the high-temperature conditions used.

Changes in fluorine content of the particles, as a result of the test, also are listed in table II. The fluorine contents listed for the particles in the as-received condition vary somewhat from those listed in table I for the same lots of particles because the analyses were performed at different laboratories using different techniques. (See appendix B for a discussion of fluorine analysis problems.) Since the high-temperature test caused relatively small changes in the fluorine content of the particles, the fluorides must be well entrapped within the tungsten coatings; thus, high-temperature annealing would not be an effective way to remove residual fluorides from vapor-deposited tungsten.

The coated particles also were metallographically examined, and representative particles from each lot evaluated are shown in the as-received and the as-tested conditions in figure 2 for the 2500°C test. All three types of particles appear similar in the as-received condition with the coatings exhibiting a fine-grained columnar structure typical of vapor-deposited tungsten. After the 2500°C test, all the particles exhibited an apparent densification of the UO_2 substrate. Some of the apparent densification is undoubtedly due to coalescence of the many small pores into the few larger voids shown; however, the restraining effect of the coating at elevated temperatures may have actually produced some fuel densification by a pressure-aided sintering mechanism.

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All three types of particle coatings exhibited appreciable grain growth as a result of the 2500° C tests. In addition, the coatings produced by either the fluoride or the duplex-coating processes exhibited porosity in the tungsten coatings. The porosity is thought to be the result of high-temperature vaporization of entrapped fluorides or other residual contaminants. The porosity is similar to that observed in the tungsten matrices of high-temperature-tested W-UO₂ cermets produced by hot isostatic compaction of tungsten-coated UO₂ particles (as shown in ref. 8). Although porosity in the coatings did not increase the fuel losses from the particles, the matrix porosity in W-UO₂ cermets has been shown (ref. 8) to be somewhat detrimental to the high-temperature fuel-retention characteristics of the cermets under thermal cycling conditions. In addition, this type of matrix porosity is thought to be detrimental to the high-temperature strength of the W-UO₂ cermets (as discussed in ref. 9). Since the particles produced by the chloride process did not exhibit this coating porosity, this method of coating is considered the preferred process. Note that the particles coated solely by the fluoride process exhibited no more porosity than those coated by the duplex-coating process even though the fluorine contaminant levels were greatly different (1280 and 40 ppm, respectively, in the as-coated condition). Thus, the amount of porosity is not directly related to the fluorine concentration and this suggests that the form of the fluorine contaminants is the more important factor. For example, in the duplex-coating process, all the 40-ppm fluorine content was probably associated with tungsten oxyfluoride within the coating. However, in the particles coated solely by the fluoride process, most of the 1280-ppm fluorine contamination could have been associated with uranium fluorides formed at the coating-substrate interface with only a small portion of the total fluorine content present as tungsten oxyfluorides within the coatings. Thus, the oxyfluoride content of the two types of particles could have been similar, and only this type of impurity may contribute to the observed porosity. Based on this premise, the oxyfluoride contaminants appear to be more detrimental to the high-temperature performance of tungsten-coated UO₂ particles than do uranium fluoride interface contaminants.

The fact that porosity was generated in the coated particles even though they contained only about 40-ppm fluorine indicates that the previously established maximum halide limit of 75 ppm is not restrictive enough with respect to fluorine contamination to assure pore-free coatings at high temperatures. More recent coated particles produced by the duplex-coating process and containing about 25-ppm fluorine (lot 8-30-66D, table I) were similarly tested at 2500° C to determine a better upper limit. Microstructures of these particles are shown in figure 3 in the as-received and the as-tested conditions. Most of the coatings on the particles were cracked, but none of the UO₂ was lost. Since UO₂ exposed to this test atmosphere at 2500° C would have been lost by vaporization, it is concluded that the thinner coatings on these particles were cracked during metallographic preparation.

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The most important observation from the microstructures of these particles is that porosity was not generated in the coatings. Therefore, it appears that adequate coatings can be produced by the duplex-coating process provided that the fluorine content is of the order of 25 ppm or less. This conclusion is important in view of the fact that UO_2 particles apparently can be tungsten coated by the duplex-coating process at less cost than by the chloride-coating process. It is of particular importance to thermal reactor concepts involving W- UO_2 cermet fuel elements since the isotopically enriched tungsten (W^{184}) required in reactors of this type would probably be produced (by gaseous diffusion) in the form of WF_6 which could be used directly in the fluoride-coating portion of the duplex-coating process.

Recommendations for Future Work on Coated Particles

The results of this study indicate that, at the current state of development, the chloride-coating process is the best particle coating method of those studied for consistently producing high-quality tungsten-coated UO_2 particles. Thus, optimization of the chloride-coating process is recommended. Because of the apparent coat savings associated with the fluoride-coating process, however, further study of the fluoride- and the duplex-coating methods also is desirable. Such a study should be aimed at better understanding the role of impurities and their effects on the high-temperature performance of coated particles and should be used to provide better control of the deposition conditions. Improving the analytical techniques (as discussed in appendix B) also should be an important part of the study.

During the current investigation, inhomogeneous qualities in particles from the same lot occasionally were observed by chemical analysis and metallographic examination of particles coated by the duplex process (lot 9-30-65A, table I) indicated considerable differences in coatings of different particles after the 2500°C test. As can be seen in figure 4, the coatings on some particles from this lot exhibited porosity while others were nearly pore-free. In addition, a difference in grain size of the tungsten coatings was apparent. The inhomogeneity was traced to the fact that the vendor produced this lot of particles from four smaller batches, which could have been coated under slightly different conditions. To avoid this problem in future evaluation and applications of coated particles, we recommend that all coated particles used in the same study be produced in a single lot.

We also recommend that work be undertaken to develop a method of producing tungsten-coated UO_2 particles with dispersed submicron thorium dioxide (ThO_2) particles in the tungsten coating. This type of coated particles could be used to produce W- UO_2 cermets with a thoriated matrix. Cermets of this type produced from mix-

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tures of W, UO_2 , and ThO_2 powders have been reported to have better strength (ref. 9) and fuel-retention characteristics (ref. 10) than nonthoriated cermet s produced by the same method. Therefore, similar gains probably could be made in cermet s produced from coated particles if a method of producing a thoriated tungsten coating on UO_2 particles could be developed.

ROLL COMPACTION OF COATED PARTICLES

Before tungsten-coated UO_2 particles can be used in fuel elements, they must be consolidated into dense bodies. Unfortunately, ordinary powder metallurgy consolidation techniques cannot be used because the relatively large, coated particles do not sinter well. A simultaneous application of both heat and pressure usually is required to compact the particles. One technique, meeting this requirement, is hot roll compaction, which is described in the following sections.

Process Description

The roll compaction process is quite simple in concept. An expendable can is filled with the desired powder and then hot rolled to achieve the desired densification. After rolling, the canning material is removed with an acid solution. The can design employed, the equipment used, and the basic procedure are described in the following paragraphs.

Can design. - The cans used in the study were fabricated from either unalloyed arc-cast molybdenum or from an arc-cast-molybdenum - 30-percent-tungsten alloy. Molybdenum was selected for the canning material because of its relatively good high-temperature strength, its compatibility with tungsten, UO_2 , and hydrogen (the atmosphere used in rolling), and the fact that it can be easily removed from the W- UO_2 cermet s with a nitric acid solution.

The basic can design evolved in this study is shown in figure 5. The width and length of the can and the thickness of the spacers may be varied to produce finished cermet s of different sizes. The majority of the cans used throughout the investigation, however, contained a 1.0- by 3.5- by 0.060-inch (2.5- by 8.9- by 0.15-cm) cavity, which yielded a finished plate (after decanning) about 1.0 inch (2.5 cm) wide by 5.0 inches (12.7 cm) long by 0.020 inch (0.05 cm) thick.

The can was fabricated by gas-tungsten arc- (TIG) welding the 0.020-inch (0.05-cm) thick face plates to the spacer plates along three sides. Filling the cans was accom-

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plished through the unwelded end, which subsequently was closed with a molybdenum plug after a hydrogen cleaning operation.

Equipment. - The canned particles were hydrogen cleaned in a molybdenum-wound tube furnace prior to compaction. A slightly flowing (approximately $1 \text{ ft}^3/\text{hr}$ ($2.8 \times 10^{-2} \text{ m}^3/\text{hr}$)) hydrogen atmosphere (17 psia (117 kN/m^2)) was maintained in the furnace during the cleaning operation.

The roll compaction operation was performed with a 4 high rolling mill having 8-inch (20-cm)-wide work rolls fabricated from an AISI H 12 tool steel. Sticking of the hot can assemblies to the steel roll was minimized by the use of high rolling speeds (200 ft/min (60 m/min)) and oxidized roll surfaces. Heating of the can assemblies to the rolling temperature was accomplished in a hydrogen atmosphere induction furnace mounted directly in front of the rolling mill. The can assemblies were pushed through the furnace into the rolls and then into a hydrogen atmosphere runout table. (This equipment is described in detail in ref. 1.)

Consolidation procedure. - During the filling of the cavity in each can with tungsten-coated UO_2 particles, the can assemblies were held upright in a jig on a vibrating table. Packed densities of about 65 percent of theoretical were achieved. After filling, the can assemblies were heated in the cleaning furnace to 1100°C at a rate of 550°C per hour, held at 1100°C for 2 hours, and then furnace cooled. The cleaning temperature of 1100°C was selected because this temperature was high enough to remove most surface oxides on the particles yet low enough to prevent excessive grain growth in the molybdenum cans. No attempt was made to optimize either the cleaning time or the temperature.

A tight-fitting molybdenum plug was used to close the opening in the can after the cleaning operation. The plug bonded to the can during rolling. The can assembly was heated in the rolling mill furnace to the desired temperature and was rolled using a pre-determined reduction schedule. The effects of both rolling temperature and schedule are discussed later.

After working, the molybdenum canning material was removed with a 1:1 hot nitric acid solution. The solution rapidly dissolved the molybdenum but did not appear to attack the tungsten- UO_2 cermet. Approximately 30 minutes were required to remove all the canning material from the cermet.

The surface finish of the cermets was improved by additional rolling after decanning using a rolling temperature of 1950°C (ref. 1).

Effect of Rolling Temperature

An effort was made to determine the optimum rolling temperature for the consolidation of tungsten-coated UO_2 particles by investigating rolling temperatures from 1200°

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to 2050° C. Several cans were rolled at each temperature using an arbitrary reduction schedule of 10-percent reduction in area on the first pass, followed by 20-percent reductions on all subsequent passes until a total reduction of about 50 percent was achieved. Both types of canning material (i. e. , unalloyed molybdenum and molybdenum - 30-percent tungsten) were used. The coated particles contained a nominal 20-volume-percent fuel loading, and the UO₂ particle size was 30 to 70 microns.

Rolling characteristics. - Observations on the can assemblies during rolling indicated that the lower the rolling temperature, the better the behavior of the canning material. At rolling temperatures above 1750° C, grain growth of the canning material became excessive, and the cans tended to crack. At the highest temperature investigated, 2050° C, the rolls became coated with flakes of molybdenum. Both canning materials yielded similar results. Apparently, the addition of 30-percent tungsten to molybdenum did not inhibit the grain growth of the canning material to any appreciable extent.

Density. - After compaction, the densities of the cermets were measured by a water-displacement technique. The results of the measurements are plotted against the rolling temperature in figure 6. These data indicate that maximum densification was achieved at rolling temperatures in the range of 1600° to 1750° C.

The somewhat lower densities attained at higher temperatures are thought to be associated with the cracks in the cans as a result of excessive grain growth at high temperatures and the fact that at the higher temperatures the canning materials are probably softer than the partially dense W-UO₂ cermet. Both factors could result in less pressure being transmitted to the cermet during rolling. In the lower temperature range (1300° to 1600° C), the cermets in the molybdenum alloy cans densified more than those in the unalloyed molybdenum cans. It is probable that the higher-strength molybdenum alloy can permitted transmission of higher rolling pressures to the cermet.

Microstructures. - Representative microstructures of cermets compacted at various temperatures are shown in figures 7 and 8. The large black areas in the UO₂ particles of these figures and all subsequent figures are thought to be the result of pullout during metallographic preparation. The density of the cermets, as evidenced by the amount of porosity in the microstructures in figure 7, increased with increasing rolling temperature up to 1750° C. Very little difference in porosity, however, could be observed between the sample rolled at 1750° C (fig. 7(c)) and the sample rolled at 2050° C (fig. 7(d)). The nonuniform appearance of the edges of the sample rolled at 2050° C (fig. 7(d)) is thought to be the result of the can developing cracks at the high rolling temperature. At the lowest temperature investigated, 1200° C, only slight bonding and deformation of the particles was achieved as shown in figure 7(a).

Examination of the rolled cermets in the etched condition at a higher magnification (fig. 8) gave some indication of the effect of temperature on particle-to-particle bonding and on grain growth in the tungsten matrix. Very little particle bonding was observed

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in the samples rolled at 1200°C (fig. 8(a)). The majority of the particle interfaces were outlined by fine grained regions, and only slight grain growth occurred across the interfaces. The tungsten matrix shows evidence of recrystallization from the typical columnar structure of vapor-deposited tungsten to a more nearly equiaxed structure.

Increasing the rolling temperature to 1450°C (fig. 8(b)) appeared to increase the particle bonding; however, most of the interface could still be detected. At 1750°C (fig. 8(c)), grain growth occurred across some of the particle interfaces, and good bonding generally was achieved. Some grain growth occurred in the tungsten, and the resulting duplex grain structure can be seen. The particle interfaces in the specimens rolled at 2050°C (fig. 8(d)) are impossible to detect in many cases.

The duplex grain structure (fig. 8(c)) was completely eliminated upon heating the sample for 2 hours at 2500°C (fig. 9). No attempt was made to determine the effect of intermediate times or temperatures. The grain size of the tungsten matrix in the heated samples is comparable to that of the cermet rolled at 2050°C (fig. 8(d)). In addition, the high-temperature treatment removed all traces of particle interfaces.

Discussion and summary of rolling temperature effects. - The results of this study indicated that higher rolling temperatures yield better particle bonding. At the higher rolling temperatures, however, the molybdenum cans tended to crack during rolling because of excessive grain growth. A compromise, therefore, was necessary, and 1700°C was selected as the rolling temperature for the rest of this investigation.

Since the molybdenum - 30-percent-tungsten alloy cans offered no apparent advantage over unalloyed molybdenum, the unalloyed molybdenum cans were used throughout the remainder of the study. If, however, a high-strength canning material could be found which would resist grain growth during working at very high temperatures, rolling temperatures in excess of 1700°C would be feasible and perhaps desirable. The reduction schedule used in the study yielded excellent results, and no attempt was made to improve it.

Effect of Total Amount of Reduction

Determination of the effect of working on the density of the cermets and on the degree of UO_2 particle elongation was of particular interest in this study since these variables are known to affect the properties of tungsten- UO_2 cermets (ref. 1). The objective of this portion of the investigation was to achieve the maximum density with the minimum amount of UO_2 particle elongation in order to maintain nearly isotropic properties. It was also of interest to determine when the cermets should be decanned and how much the cermets should be worked in the decanned condition.

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The cans and coated particles used in the study were similar to those used previously in the study of rolling temperature, except that only unalloyed molybdenum cans were employed. All rolling of the canned particles was performed at 1700°C . The can assemblies were rolled various amounts (from 20- to 80-percent total reduction) using the reduction schedule discussed in the previous section.

Rolling characteristics. - The amount of working at 1700°C had no apparent effect on the condition of the molybdenum cans, and no problems were encountered during rolling. Even after 80-percent reduction in thickness, very few cracks could be detected in the cans. The surface of the tungsten- UO_2 cermets, however, became more irregular with increasing amounts of work. The irregularities can probably be attributed to the increasing difference in hardness between the molybdenum can and the tungsten- UO_2 cermet as the density of the cermet increased with working.

A comparison of the amount of reduction of the can assemblies (in percent) with the reduction of the composite (in percent) indicated that the cermets were reduced about 5 percent more in thickness than were the can assemblies. For example, reducing the can assembly 50 percent in thickness resulted in a 55-percent reduction in the cermet thickness. Apparently, during initial rolling, the low-density (~ 65 percent of theoretical) cermet compacted more easily than the stronger molybdenum deformed. The deformation of the can and cermet became more uniform, however, as the density and the strength of the cermet increased with working.

Working of the cermets resulted in a rapid increase in density as shown in figure 10. Full densification was achieved after about 65-percent reduction in plate thickness. Measured densities slightly in excess of theoretical are probably attributable to slight differences between the actual fuel loadings of the cermet and those assumed for the density calculations.

Microstructures of the tungsten- UO_2 cermets at different stages of rolling are shown in figure 11. The photomicrographs corroborate the results of the density measurements previously discussed. Porosity can be seen in the tungsten matrix of the samples which were reduced 55 percent or less, whereas cermets reduced 65 percent or more appear fully dense.

Working the cermets had little influence on the deformation of the UO_2 particles until the gross voids in the cermets, as shown in figures 11(a) and (b), were eliminated. With increased working, the UO_2 particles deformed appreciably (figs. 11(c) to (f)). The UO_2 particles in the first fully dense cermet in the series (fig. 11(d)) have major- to minor-axis ratios of about 10 to 1. For this particular particle size and fuel loading, this ratio represents the minimum amount of particle deformation achievable in the fabrication of fully dense tungsten- UO_2 cermets by the roll compaction process at its current state of development.

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Decanning and subsequent rolling. - The surfaces of the tungsten- UO_2 cermets after decanning were irregular as a result of the coated particles indenting the molybdenum canning material during rolling. Thus, additional working after decanning was desirable to improve the surface finish of the plates. The following study was conducted to determine at what point in the rolling schedule the cermets should be decanned. In the canned condition, the cermets were rolled various amounts using the procedures described previously. After decanning, the cermets were rolled additional amounts at 1950°C using a reduction schedule of 10 percent per pass. The densities of the cermets worked in the decanned condition were compared to the densities of the cermets rolled a similar amount in the canned condition. The effect of the decanning schedule on the fuel-retention characteristics of the cermets also was determined.

The results indicated that in all cases, the densities of the cermets worked in the decanned condition were slightly lower (1 to 2 percent) than the densities of the canned cermets after an equivalent amount of working. The reason for this difference is uncertain, but possibly the canning material permitted a more uniform stress distribution during rolling which resulted in higher densities. In addition, the canning material might have minimized cooling of the cermets during rolling.

Fuel-retention studies on the tungsten- UO_2 cermets at 2500°C in flowing hydrogen indicated that working the composites in the decanned condition resulted in higher fuel losses, with the amount of fuel loss being related to the amount of working. Fuel losses as high as 11 percent after 10 hours at temperature were measured on composites reduced 50 percent in thickness in the decanned condition. Metallographic examination of these samples (fig. 12) indicated that the majority of the fuel was lost from the surfaces of the cermets. Apparently, severe working of the cermets in the decanned condition tended to crack the tungsten coatings of the surface particles. The UO_2 in these particles then was free to vaporize from the samples at elevated temperature. Composites reduced 20 percent in the decanned condition had fuel losses of less than 1 percent, which were comparable to the fuel losses observed for the composites worked only in the canned condition.

Discussion and summary of reduction effects. - For the fuel loading and particle size investigated, fully dense cermets could be produced by rolling the cermets at 1700°C until an overall thickness reduction of about 65 percent or greater was achieved. Working the cermets less than 65 percent resulted in incomplete densification, whereas working the cermets more than 65 percent caused excessive elongation of the UO_2 particles. Based on these results, a total reduction of about 65 percent in the thickness of the cermets was selected as the standard reduction employed for the roll compaction of tungsten-coated UO_2 particles.

Working the tungsten- UO_2 cermets in the decanned condition improved the surface finish of the samples, but severe working of this type was detrimental to the fuel-

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retention characteristics. The rolling procedure eventually selected consisted of working the cermet in the canned condition until a 60-percent reduction in thickness was attained. The cermet then was decanned and was rolled at 1950⁰ C until a total overall reduction of 65 percent was achieved.

Composite Cladding Technique

Because of the possibility of cracking the thin tungsten coating of the UO₂ particles at the surfaces of the cermet during rolling, an additional, external, unfueled tungsten cladding was desired to minimize fuel loss at elevated temperatures. This combination of an external tungsten cladding and the use of tungsten-coated UO₂ particles should result in fuel elements having a higher degree of reliability.

Various techniques including vapor deposition (ref. 5) and plasma spraying (ref. 11) have been developed in previously reported studies to clad tungsten-UO₂ cermets. For cladding plates fabricated from mixtures of tungsten and UO₂ powders by a powder-metallurgy - hot-rolling process, a roll-bonding technique was developed utilizing wrought tungsten foil (ref. 1). The purpose of the following study was to determine if roll bonding could be used to clad plates produced by the roll compaction of coated particles.

Preliminary cladding studies were conducted using a technique similar to that described in reference 1. Partially dense (~90 percent of theoretical) W-UO₂ cermets were prepared from tungsten-coated UO₂ particles by the roll compaction process. Following decanning, the surfaces of the cermet were sanded with 180 grit paper, washed with water, and rinsed with acetone. Next, the cermet was sandwiched between layers of 0.003-inch (0.0076-cm)-thick tungsten foil and was rolled at 1950⁰ C until the thickness was reduced about 50 percent. Approximately five roll passes were required to achieve this reduction. The composites produced in this manner were essentially fully dense, and the cladding apparently was bonded to the fueled core. Fuel retention studies indicated that the cladding was effective in inhibiting fuel loss: no fuel loss was metallographically detected from the composites heated to 2500⁰ C for 2 hours in hydrogen.

With the feasibility of roll cladding having been demonstrated a technique for cladding the cermet during rolling in the canned condition was investigated. In this cladding method, the inside of the molybdenum was coated with tungsten prior to roll compaction. The most promising method developed for lining the cans with tungsten involved roll bonding of tungsten foil to molybdenum sheet at 1750⁰ C. Cans were fabricated from this material with the tungsten-clad surfaces on the inside. The cans then were filled with coated particles and were rolled at 1700⁰ C to a total reduction of 65 percent. The excellent bonding achieved with this process is shown in figure 13. Some evidence of grain

growth across the core-cladding interface of the as-rolled cermet can be observed in figure 13(a).

Heating the composite to 2500° C for 2 hours resulted in greatly increased grain growth across the core-cladding interface (fig. 13(b)). In addition, the high-temperature treatment resulted in extensive grain growth of the tungsten matrix, as discussed previously. The results of fuel retention studies on these samples were similar to those obtained on the samples clad by roll bonding in the decanned condition (i. e., essentially no fuel was lost).

Process Capability

During the development of the roll compaction process, tungsten-coated UO_2 particles of various sizes and fuel loadings were consolidated into a variety of sizes. Although the samples produced do not represent the ultimate capabilities of the process, they do give some indication of the range of process capabilities.

Fuel loading. - Tungsten- UO_2 cermets having fuel loadings of 10- to 70-volume-percent UO_2 have been successfully consolidated by the roll compaction of tungsten-coated UO_2 particles. Varying the fuel loading had very little effect of the rolling characteristics of these samples. This result is in contrast to the results obtained previously on cermets produced from tungsten and UO_2 powder mixtures (ref. 1). For the latter cermets, there was an increasing tendency to crack during rolling as the fuel loading was increased up to 40-volume-percent UO_2 (the highest fuel loading investigated). Apparently, the tungsten separating each UO_2 particle reduced the cracking tendencies of the cermets produced from coated particles. An example of a roll compacted cermet containing 60-volume-percent UO_2 is shown in figure 14. Note that, even at this relatively high fuel loading, the UO_2 dispersion is uniform in both the longitudinal and the transverse directions and that each UO_2 particle is completely encapsulated in tungsten.

Particle size. - Tungsten- UO_2 cermets, each containing UO_2 particles of a different size range, were consolidated from coated particles using similar rolling parameters. The UO_2 size ranges investigated were 10 to 30 microns, 30 to 70 microns, and 70 to 130 microns. The fuel loadings of all the cermets were 35 volume percent.

No differences could be detected in the behavior of the three types of material during roll compaction. Photomicrographs of the three types of cermets are shown in figure 15. The samples produced from the 10- to 30-micron UO_2 particles (fig. 15(a)) and the 30- to 70-micron UO_2 particles (fig. 15(b)) appear to be fully dense. However, in the cermet containing the 70- to 130-micron UO_2 particles (fig. 15(c)), fine porosity is apparent throughout the tungsten matrix. This porosity is not typical of the type en-

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countered because of incomplete compaction. Instead, the porosity is thought to be the result of vaporization of impurities as discussed previously in the section on coated-particle preparation.

Plate size. - Although most of the fuel plates produced by roll compaction were about 1.0 inch (2.5 cm) wide by 5.0 inches (12.7 cm) long by 0.020 inch (0.05 cm) thick, various other plate sizes also were produced. The thickness of the plates could be easily changed by using molybdenum spacers of different thicknesses in the can assembly. The thinnest and the thickest cermet produced in the study were 0.008 inch (0.02 cm) and 0.047 inch (0.12 cm), respectively. No attempt was made, however, to determine the minimum and the maximum plate thickness attainable. An example of a 0.010-inch (0.025-cm)-thick plate (with 60-volume-percent UO_2) was shown previously in figure 14.

The length and the width of the cermets also can be changed by using various can sizes. Cermets as large as 1.5 inches (3.8 cm) wide by 8 inches (20 cm) long were routinely produced. A single attempt to produce a relatively large (4 in. (10 cm) wide by 10 in. (25 cm) long) cermet containing 20-volume-percent UO_2 was partially successful. During filling of the can with coated particles, the thin, unsupported surfaces of the can bulged outward, and thus the center portion of the can was thicker than the edges. The difference in thickness resulted in the center of the plate being reduced more than the edges during rolling. In all other respects, the sample was fabricated successfully. Although improvements in the can design are required to produce plates of this size or larger, the feasibility of roll compacting large size tungsten- UO_2 cermets was demonstrated.

CONCLUSIONS

Methods of preparing and consolidating tungsten-coated UO_2 particles were investigated in a two-part study. The first part of the study consisted of obtaining and evaluating commercially produced tungsten-coated UO_2 particles. From the results of this work, the following conclusions may be drawn:

1. The chloride-coating process (hydrogen reduction of tungsten hexachloride (WCl_6)) for the tungsten coating of uranium dioxide (UO_2) particles has demonstrated the best capability for successfully meeting the desired overall goals for high reliability coatings on UO_2 particles.

2. A duplex-coating process involving a two-layer coating produced by subsequent use of the chloride- and the fluoride-coating process appears to be an attractive alternate for producing tungsten-coated UO_2 particles more economically. However, improved control of the fluoride-coating process (hydrogen reduction of tungsten hexafluoride (WF_6)) for tungsten-coating UO_2 particles is required to overcome various problems

such as excessive amounts of fluorine impurities and porosity which develops in the coatings at high temperature.

A roll compaction technique was developed for the consolidation of tungsten-coated UO_2 particles in the second part of the study. The conclusions are summarized as follows:

1. Fully dense, tungsten- UO_2 plates can be produced from tungsten-coated UO_2 particles by the following procedure:

a. Load coated particles into flat molybdenum cans and vibratory compact to a density of about 65 percent of theoretical.

b. Clean canned particles in flowing hydrogen at 1100°C for 2 hours.

c. Roll at 1700°C until a total reduction of about 60 percent is achieved in the tungsten- UO_2 cermets.

d. Remove molybdenum canning material with 1:1 nitric acid solution.

e. Roll the cermet at 1950°C after decanning, until a total overall reduction of 65 percent is achieved in the sample.

2. The roll compaction process is relatively insensitive to fuel loading and to size of the tungsten-coated UO_2 particles. Cermets were successfully consolidated from coated particles containing up to 70-volume-percent UO_2 (the highest fuel loading studied). Tungsten - 35-volume-percent UO_2 cermets were consolidated from UO_2 particles up to 130 microns in diameter (the largest particle size studied).

3. The roll compaction process is applicable to a wide variety of plate sizes. Sizes up to 1.5 inches (3.8 cm) wide by 8 inches (20 cm) long were routinely produced.

4. The surfaces of the cermets may be clad with unfueled tungsten by roll bonding techniques. The cladding can be applied either after decanning or as a part of the can assembly during initial compaction.

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, April 5, 1967,

122-28-01-01-22.



APPENDIX A

ALTERNATE PROCESSES FOR TUNGSTEN-COATING UO_2 PARTICLES

With the early indication that particles coated by the fluoride process may not be adequate for the intended application, alternate methods of coating tungsten on UO_2 particles were concurrently investigated in an exploratory manner. The investigations were performed under three NASA-sponsored contracts. In these investigations, dense, high-purity tungsten coatings were desired, and high concentrations of carbon and halide impurities, particularly, were to be avoided. A brief summary of the results obtained from these investigations follows.

Contract C-25101A (Union Carbide Corp., Oak Ridge Gaseous Diffusion Plant)

In this investigation (reported in ref. 12) thin, dense tungsten coatings were to be applied by condensation of electron-beam evaporated tungsten on UO_2 . The vapors of the tungsten were condensed on the UO_2 as the particles were tumbled in a revolving baffled drum. This method of depositing tungsten avoided the contamination problem of either carbon or halides and provided a very thin layer of tungsten which protected the UO_2 from reaction with the halides subsequently used to vapor-deposit additional tungsten. Work on the electron-beam vaporization of tungsten was terminated because of the success achieved with the chloride- and the duplex-coating processes. However, the results were successful enough to indicate that future work on this coating process is warranted if nonhalide tungsten coatings are required.

Contract NAS3-4093 (Battelle Memorial Institute, Columbus Laboratory)

In an unpublished investigation, thin, dense tungsten coatings were to be applied on UO_2 particles using processes other than halide-vapor deposition. Three methods were investigated using fluidized bed techniques, and the significant results were as follows:

Plasma evaporation of W. - Tungsten particles were evaporated in a plasma arc jet, and the effluent tungsten plasma (and other species) was injected into a fluidized bed to be condensed on the UO_2 particles. The tungsten coatings obtained were poor in quality, being porous and weak. Since only thin coatings with poor coverage were obtained, work on this technique was terminated.

[REDACTED]

Plasma reduction of WO_3 . - Tungsten oxide coating of UO_2 particles was performed in a system using a plasma arc jet and fluidized bed similar to those used in the plasma evaporation of tungsten. Complete coverage of the tungsten coatings on the UO_2 was obtained, but only a few particles were coated. In addition, the coatings were porous and weakly bonded to the UO_2 substrate. Efforts to improve the density of the tungsten coatings by furnace treatment at 1600°C in hydrogen were unsuccessful. Work on this type coating was terminated because of the lack of encouraging results.

Pyrolysis of tungsten carbonyl $\text{W}(\text{CO})_6$. - Pyrolysis of $\text{W}(\text{CO})_6$ for the vapor deposition of tungsten is normally performed within a deposition temperature range of 260°C to about 500°C . However, the resulting tungsten is usually contaminated (because of side reactions) with large amounts of carbon or oxygen. Thermodynamic studies conducted in this investigation predicted that these impurities could be avoided if $\text{W}(\text{CO})_6$ is pyrolyzed at sufficiently high temperatures (above about 850°C) in the presence of suitable amounts of hydrogen and steam. Attempts at coating UO_2 in a fluidized bed at 1000°C did produce coatings, but the tungsten was porous and weak. It was deduced that the faulty coatings resulted from gas phase nucleation which was favored by both the higher deposition temperature and the relatively high total gas pressures (hydrostatic heads) required to maintain the fluid bed of particles. An exploratory experiment designed to reduce the occurrence of gas phase nucleation was performed by pyrolyzing the $\text{W}(\text{CO})_6$ in vacuum (0.35 torr (47 N/m^2)) with a heated tungsten wire substrate. Metallographic examination of the resulting tungsten coating demonstrated that it was nonporous and was composed of fine-grained, equiaxed crystals. The density was determined to be essentially theoretical, and the carbon impurity was found to be less than 10 ppm. It is probable that tungsten coatings of this quality on UO_2 particles would be adequate; however, such low operating pressures preclude the use of a fluidized-bed technique. Thus, development of other methods capable of agitating the particles during the coating process at the low pressure would be required. Further work on the carbonyl process was terminated because of the success achieved by then with halide-vapor deposition.

Contract NAS3-4284 (General Technologies Corporation)

In this unpublished investigation, thin, dense tungsten coatings were to be applied on UO_2 particles using tungsten iodide (WI_2) and $\text{W}(\text{CO})_6$ methods. The processes were to be investigated with fluidized bed techniques; the results of the investigations are as follows:

Tungsten iodide. - Two methods of vapor deposition were to be used to obtain tungsten coatings from WI_2 : (1) thermal decomposition and (2) hydrogen reduction. The

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WI₂ was to be prepared in situ during operation of the fluidized beds. However, unresolved difficulties were encountered in forming the WI₂, and no tungsten coatings were obtained.

Tungsten carbonyl. - On the basis of the results from the thermodynamic studies performed under contract NAS3-4093, several batches of UO₂ particles were coated with tungsten at pressures as low as support of the fluidized bed of particles would permit, about 30 torr (4000 N/m²). Deposition temperatures ranged from 400° C to about 1200° C. At the higher deposition temperature, the formation of soot at the cooler, entrant portion of the bed was severe enough to cause frequent plugging. The soot also became a source for carbon contamination in the particles due to abrasive action of the agitated particles during fluidization. Soot formation was avoided only when the lower temperature, 400° C, was used. Metallographic examination of the coated particles showed the coatings were not satisfactory because of carbide formations in the tungsten which caused the coatings to be fragile and weak. Work on the carbonyl process was terminated because of the success being achieved with halide-vapor deposition.

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APPENDIX B

CHEMICAL ANALYSIS OF TUNGSTEN-COATED UO_2 PARTICLES

The tungsten-coated UO_2 particles used in the studies described in this report were procured to a purity specification of 99.9-percent minimum purity with no single metallic element exceeding 200 ppm, carbon not exceeding 30 ppm, and total halide not exceeding 75 ppm. Extensive chemical analyses were conducted on several lots of coated particles using the analytical techniques described in reference 13, and analyses for three representative lots of particles are tabulated in table III along with a typical analysis for the UO_2 substrate particles used to produce the coated particles. The analyses show that good control of metallic impurities was attained with only iron, nickel, and chromium consistently appearing at appreciable levels in the particles coated by either the chloride- or duplex-coating process. The source of the contaminants was traced to the stainless-steel containers and hardware used for the tungsten hexachloride. Analysis of more recently produced coated particles indicates that better control of the starting materials results in much lower levels (<30 ppm) of the metallic contaminants.

As discussed in the section High-Temperature Evaluation of Coated Particles (p. 6) of this report, the most significant nonmetallic impurity found in the coated particles was fluorine. Unfortunately, this impurity has also posed the most difficult analytical problems as demonstrated by widely different analytical values obtained on similar samples. For example, selected samples of coated particles were sent to three independent laboratories for fluorine analysis. Each laboratory analyzed three different batches of coated particles that were representative of different fluorine levels. Considerable effort was exercised to ensure selection and control of the similar samples for each laboratory; however, it must be recognized that coated particles may vary within the same lot, and thus some inhomogeneity may have existed in the samples. All three laboratories used a pyrohydrolysis, colorimetric analytical method with minor differences in procedure. The resultant fluorine values are listed in table IV. The data from the three laboratories show good agreement for the particles with low fluorine content (sample A). However, at the higher fluorine contents in samples B and C, the agreement is poor, even though laboratories 1 and 2 used almost identical methods of analysis. Based on these differences in results, it appears that an improved method of analysis is needed for reliably determining the amount of fluorine in tungsten-coated UO_2 particles.

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TABLE I. - HALIDE IMPURITY OF TUNGSTEN-COATED UO_2 PARTICLES

Coating process	Lot	Vendor	Nominal W-coating thickness, μm	Halide impurity	
				Fluorine, ppm	Chlorine, ppm
Fluoride (H_2 reduction of WF_6)	8-31-62	A	10	2200	---
	6-4-63	A	3	300	---
	9-30-65D	A	12	1100	12
	8-28-63B	B	10	3000	---
	12-3-63A	B	3	1400	---
	12-3-63B	B	15	450	11
	L-1 to 8	C	10	^a 808	^a 16
	L-1	D	25	112	12
	L-2	D	10	550	20
	2993-43	E	10	265	11
Chloride (H_2 reduction of WCl_6)	10-14-64	A	4	<2	40
	11-12-65B	A	11	<10	16
	10-16-64	F	4	55	3
Duplex (H_2 reduction of $WCl_6 + H_2$ reduction of WF_6)	9-30-65A	A	10	64	2
	9-30-65B	A	8	48	<2
	9-30-65C	A	5	120	2
	L-3	D	10	430	440
	8-30-66D	A	6	25	46

^aHalide values are averages from 8 lots produced by this vendor.

TABLE II. - EFFECT OF HIGH-TEMPERATURE TESTS
ON TUNGSTEN-COATED UO_2 PARTICLES

Coating process	Test ^a temperature, $^{\circ}C$	Uranium dioxide loss, weight percent	Fluorine content	
			As-received, ppm	As-tested, ppm
Fluoride	2500	0.68	1280	1160
Duplex	2500	.75	40	18
Chloride	2500	.91	^b 5, 30	<5
Chloride	2000	.23	^b 5, 30	----
Chloride	1500	.03	^b 5, 30	----

^aFor 1 hr in hydrogen.

^bResults of duplicate analyses.

TABLE III. - CHEMICAL ANALYSES OF TUNGSTEN-COATED UO_2 PARTICLES

COATED BY HALIDE-VAPOR DEPOSITION TECHNIQUES

Amount (ppm, except as noted)

Element	UO_2 substrate ^a (typical of material before cladding)	Tungsten-coated UO_2 particles (as-received condition)		
		Fluoride process lot 12-3-63B	Chloride process lot 10-14-64	Duplex-coating process lot 9-30-65A
Tungsten	(b)	88.5 percent	^c 46.0 percent	76.5 percent
Uranium	88.12 percent	9.93 percent	47.7 percent	20.1 percent
Oxygen	^c 11.86 percent	(b)	(b)	(b)
Fluorine	^d <5	400	<2	64
Chlorine ^e	7	11	40	2
Carbon	(b)	15	17	41
Nitrogen	24	76	11	27
Sulfur	<1	<2	<1	1
Aluminum	100	<1	<1	2
Antimony	<1	(b)	<1	<1
Arsenic	<30	<10	<10	(b)
Barium	<10	<3	<3	<3
Beryllium	<1	<.1	<.1	<.1
Bismuth	<1	<.5	<.5	<.5
Boron	<.1	<.1	.5	2
Cadmium	<.2	<1	<1	<1
Calcium	1	<1	2	<1
Chromium	10	<1	100	50
Cobalt	<1	<5	<5	<5
Copper	1	<1	<1	1
Cesium	<10	<10	<10	<10
Gallium	<1	<5	<5	<5
Germanium	<1	<1	<1	<1
Hafnium	<1	<2	<2	<2
Indium	<3	<1	<1	<1
Iron	10	<1	70	20
Lead	<3	<1	<1	<1
Lithium	<1	<1	1	<1
Magnesium	5	<1	<1	<1
Manganese	<1	<1	<1	<1
Mercury	<1	<2	<2	<2
Molybdenum	20	3	<2	4
Nickel	<1	<1	25	100
Niobium	2	<2	4	<2
Potassium	<5	10	<1	50
Rubidium	<10	<10	<10	<10
Silicon	2	<1	2	<1
Silver	<.1	<1	<1	<1
Sodium	8	<1	<1	<1
Strontium	<5	<1	<1	<1
Tantalum	<.5	<4	<4	<4
Thallium	<2	<1	<1	<1
Tin	<.5	<1	<1	<1
Titanium	2	<2	2	2
Zinc	<20	4	<10	<10
Zirconium	20	4	6	<2

^aAdditional information on UO_2 , O/U ratio, 2.006; density, 10.34 g/cm^3 ; sieve analysis, +270 mesh (0.62 percent), -270/+400 mesh (94.90 percent), -400 mesh (4.48 percent).

^bValue not determined.

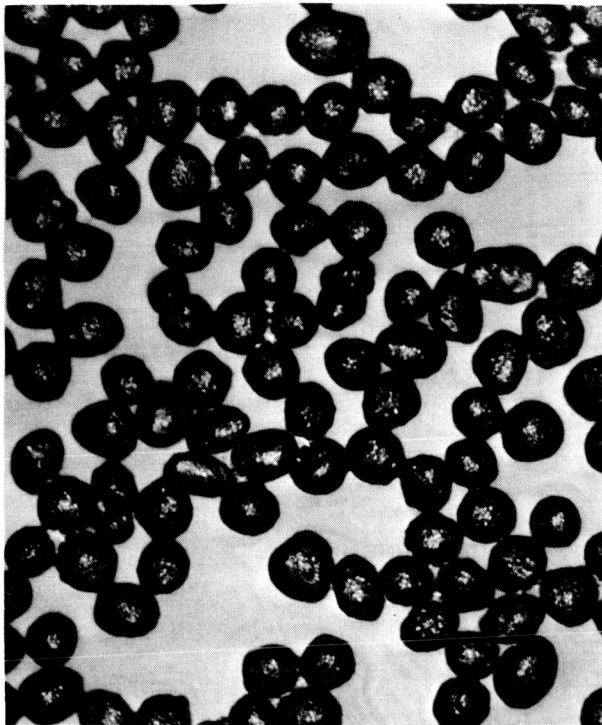
^cValue computed by difference or by stoichiometry, as applicable.

^dValue not determined, but typically <5 ppm for other similar UO_2 products.

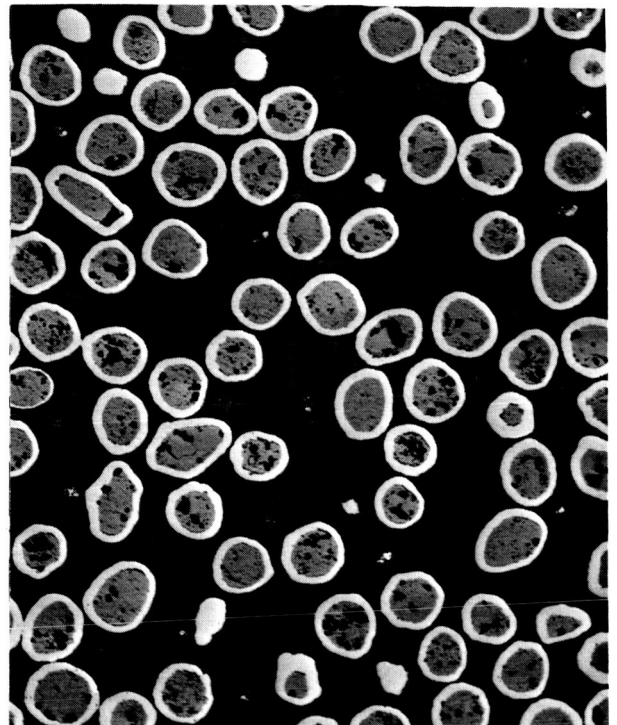
^eValue is the total impurity content for Cl, Br, and I.

TABLE IV. - DETERMINATION OF FLUORINE
IN TUNGSTEN-COATED UO₂ PARTICLES

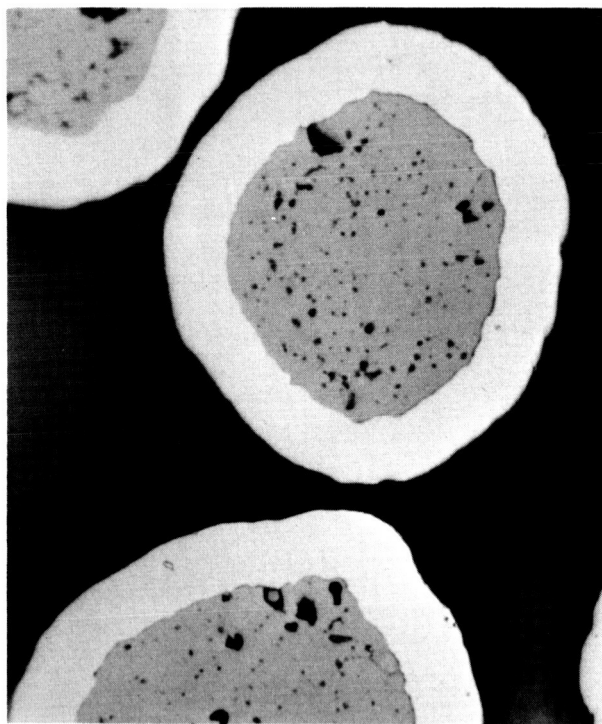
Laboratory	Fluorine, ppm		
	Sample A	Sample B	Sample C
1	1, 3, 3	73, 47, 51	107, 128, 111
2	<5	33, 30	73, 67, 67
3	<5, <5, <5	26, 33, 29	92, 104, 97



(a) Exterior view. X100.



(b) Cross section, unetched. X100.

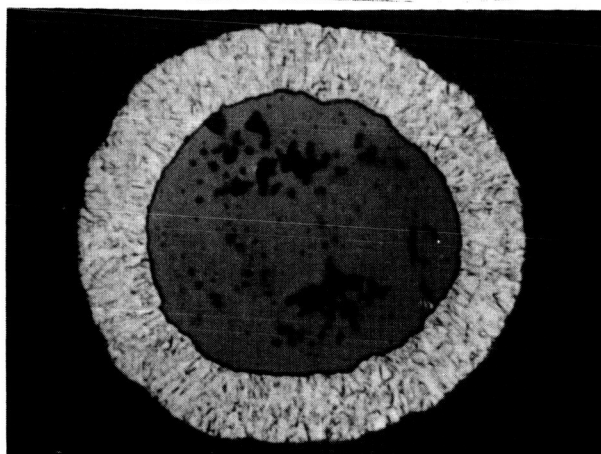


(c) Cross section, unetched. X750.

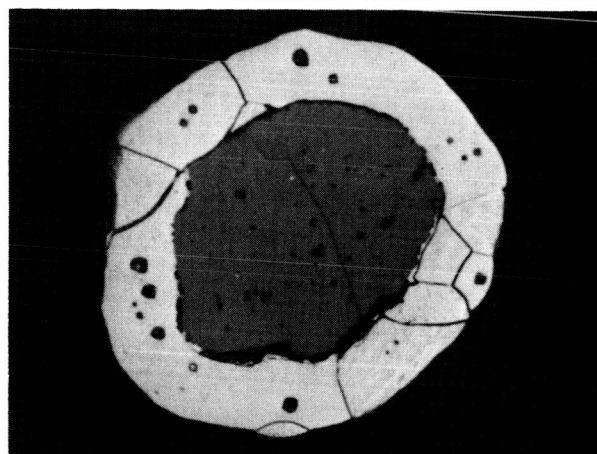


(d) Cross section, etched with Murakami's reagent. X750.

Figure 1. - Typical examples of tungsten-coated UO_2 particle prepared by fluoride process. Coating thickness about 15 microns. Particle lot 12-3-63B.

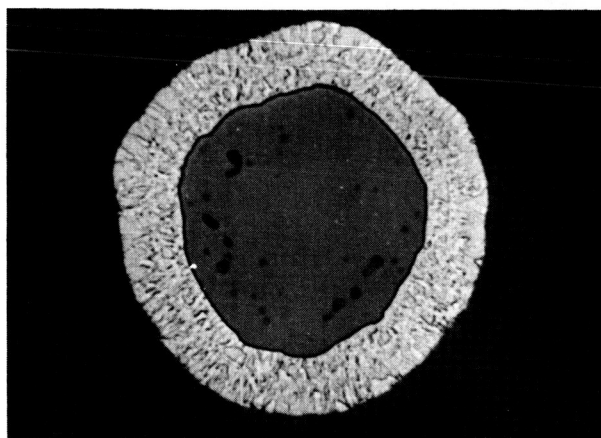


Before heating (F, 1280 ppm)

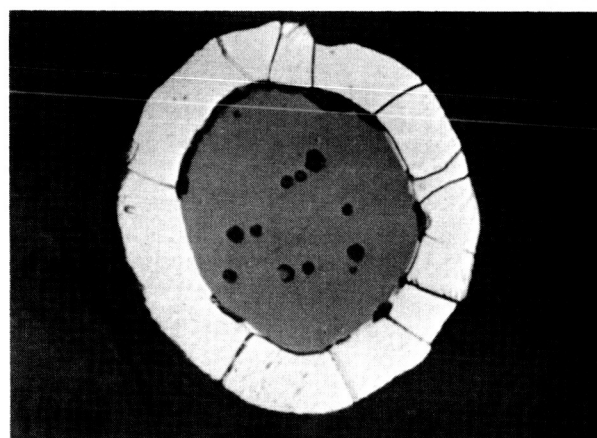


After heating (F, 1160 ppm)

(a) Lot 9-30-65D, coated by fluoride method.

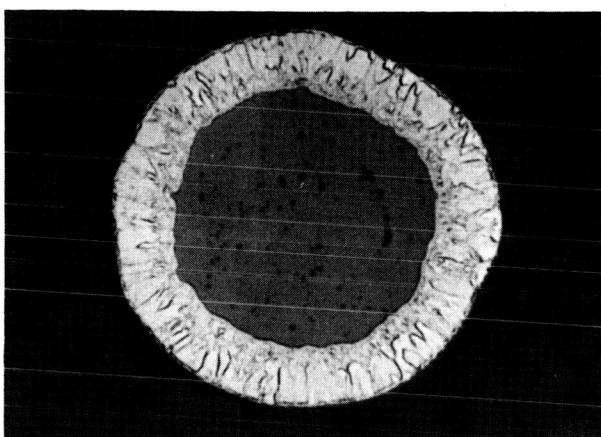


Before heating (F, 5 to 30 ppm)

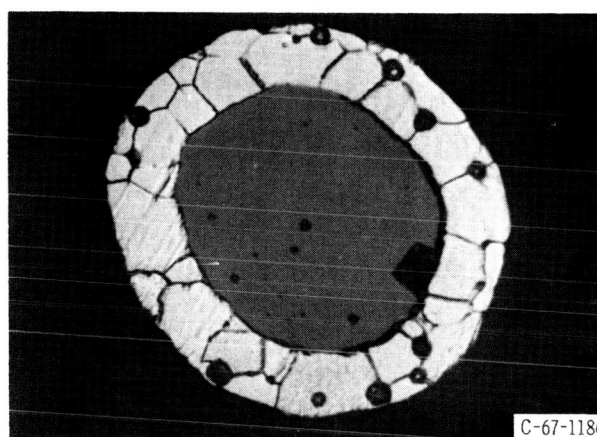


After heating (F, <5 ppm)

(b) Lot 11-12-65B, coated by chloride method.



Before heating (F, 40 ppm)



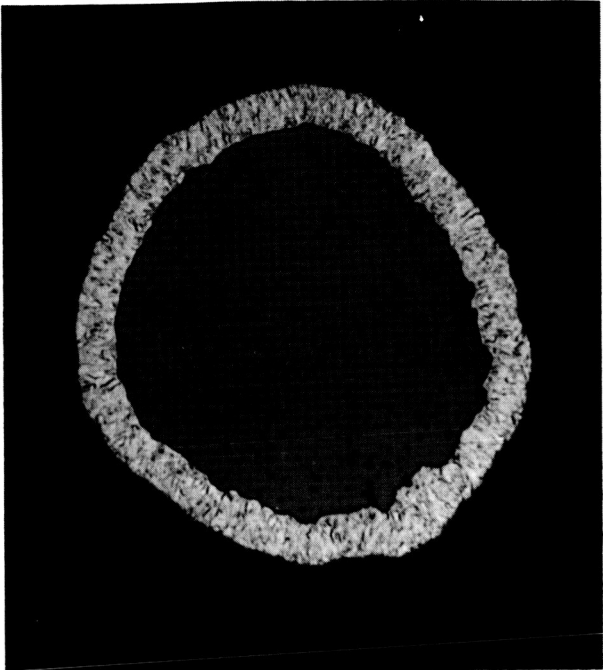
After heating (F, 18 ppm)

(c) Lot 9-30-65B, coated by duplex-coating process.

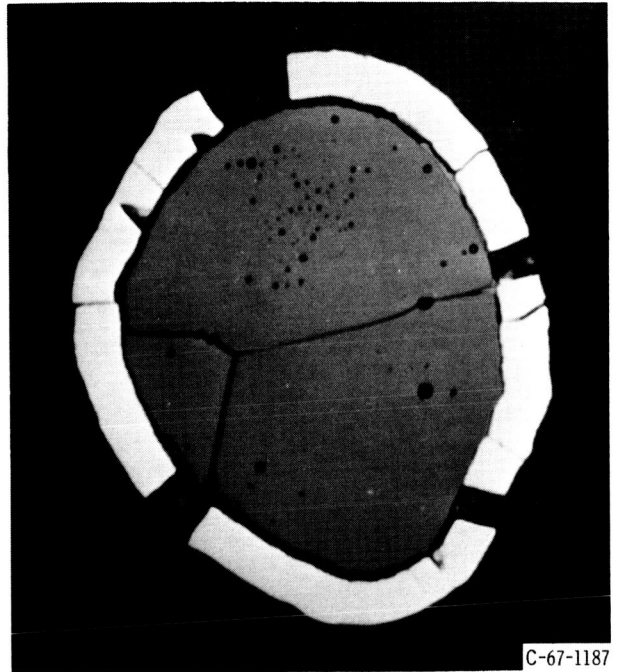
C-67-1186

Figure 2. - Effect of heat treatment on microstructure of vapor-deposited tungsten-coated UO_2 particles. Heat-treating condition, 2500°C in flowing hydrogen for 1 hour. Etched with Murakami's reagent; X750.

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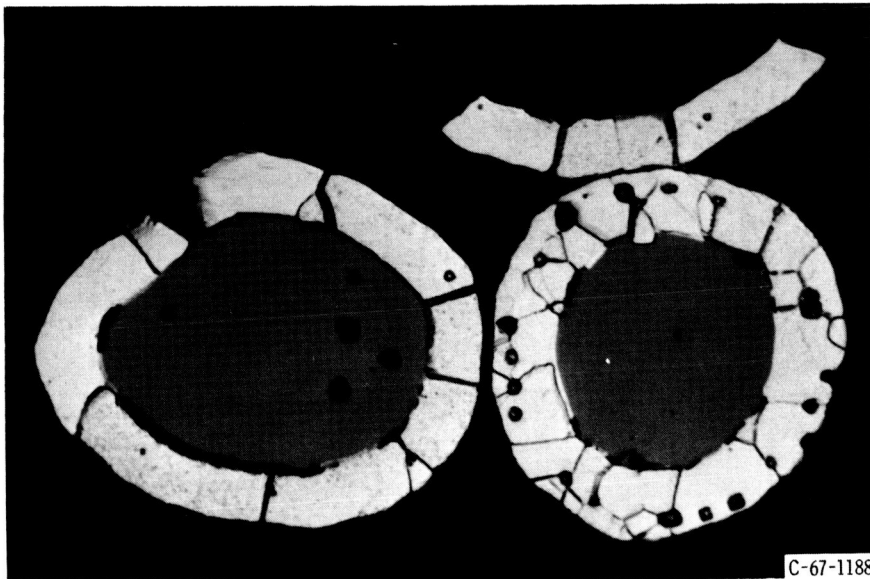
(a) Before testing (F, <25 ppm).



C-67-1187

(b) After testing (F, <10 ppm).

Figure 3. - Effect of heat treatment (1 hr, 2500° C, flowing hydrogen) on microstructure of coated particle lot 8-30-66D, coated by duplex-coating process. Etched with Murakami's reagent; X750.



C-67-1188

Figure 4. - Examples of nonuniform quality in coated particle products from same lot after testing at 2500° C in flowing hydrogen for 1 hour. Particle lot 9-30-65A, duplex-type tungsten coating on UO₂ particles. Etched with Murakami's reagent; X750.

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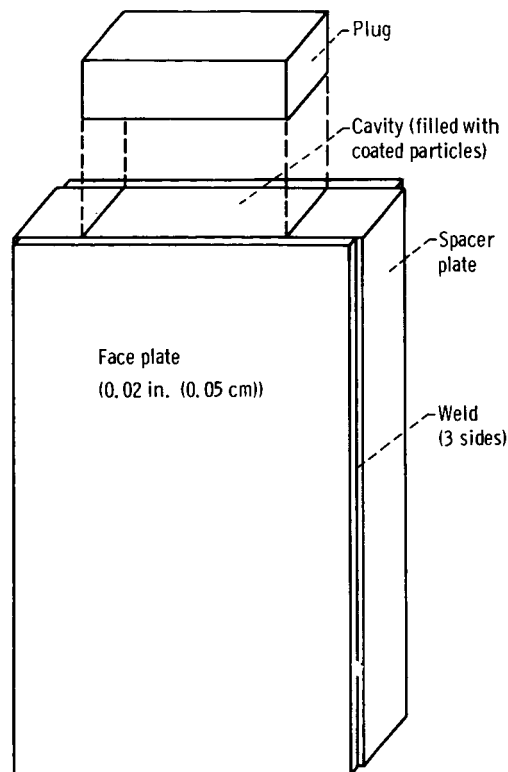


Figure 5. - Basic can design used for roll compaction of tungsten-coated UO_2 particles.

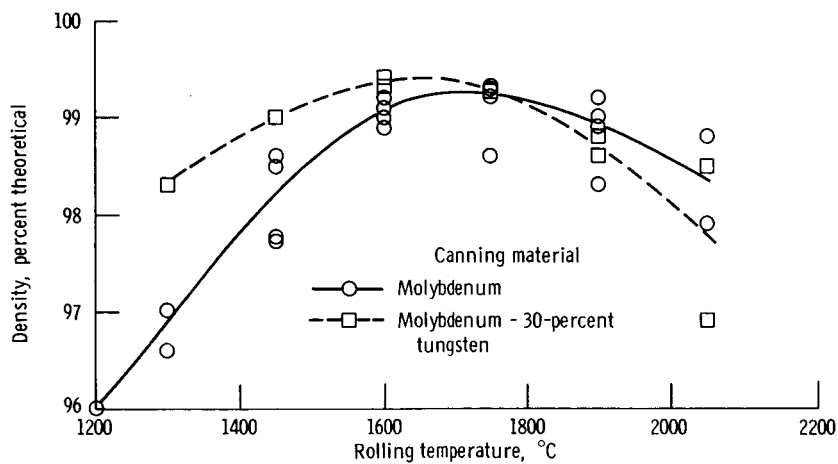
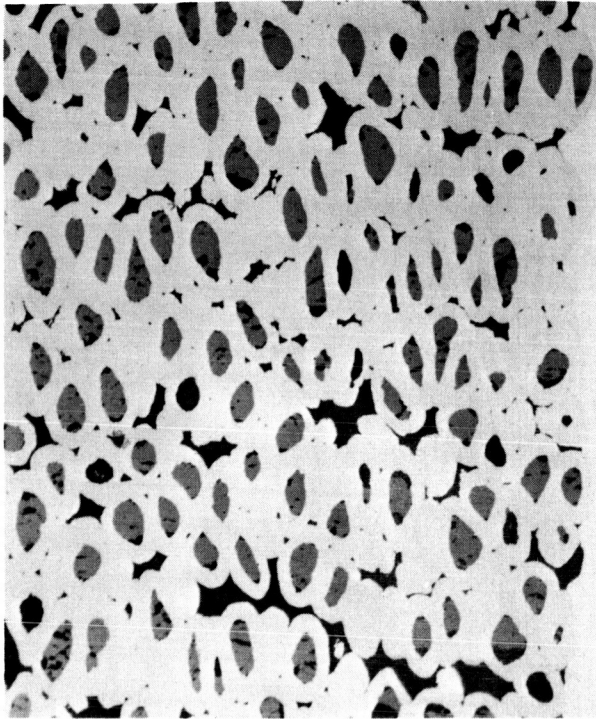
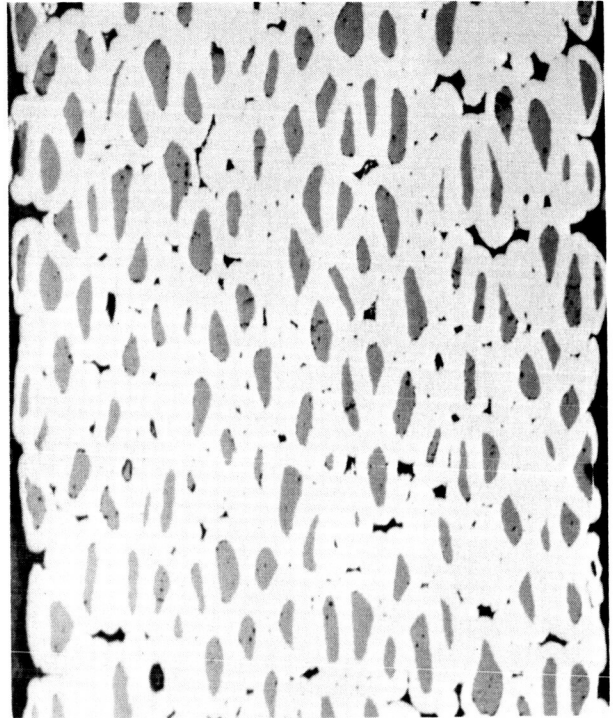


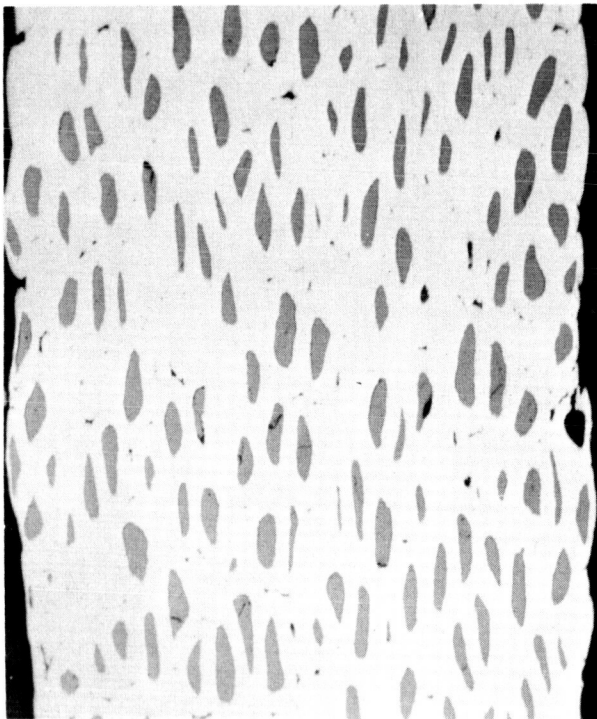
Figure 6. - Effect of rolling temperature on density of tungsten - 20-volume-percent- UO_2 plates consolidated from tungsten-coated UO_2 particles. Can assemblies worked 50 percent.



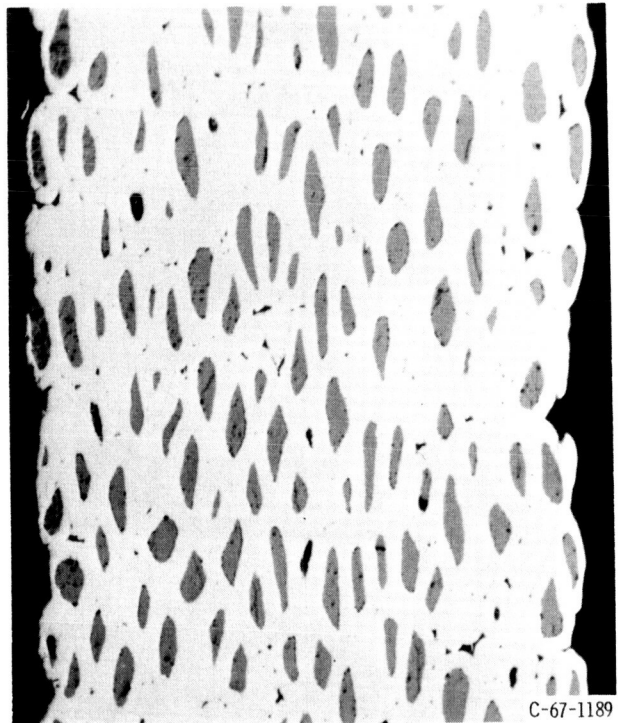
(a) Rolled at 1200° C.



(b) Rolled at 1450° C.

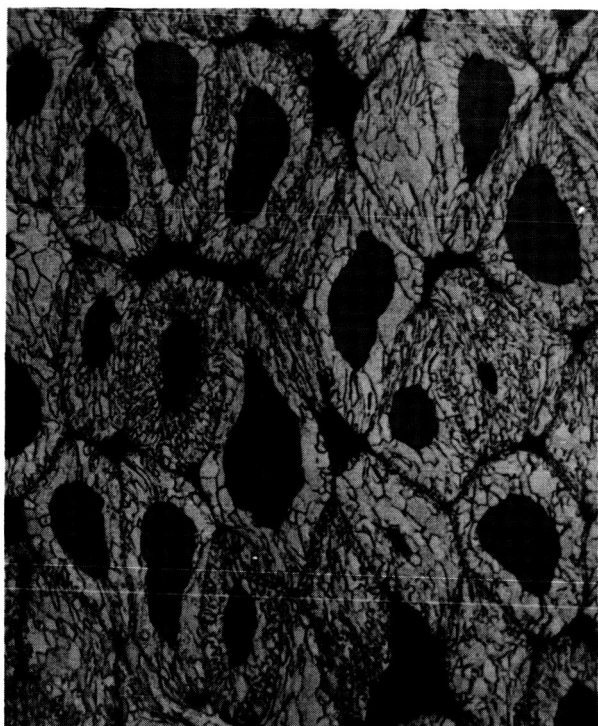


(c) Rolled at 1750° C.

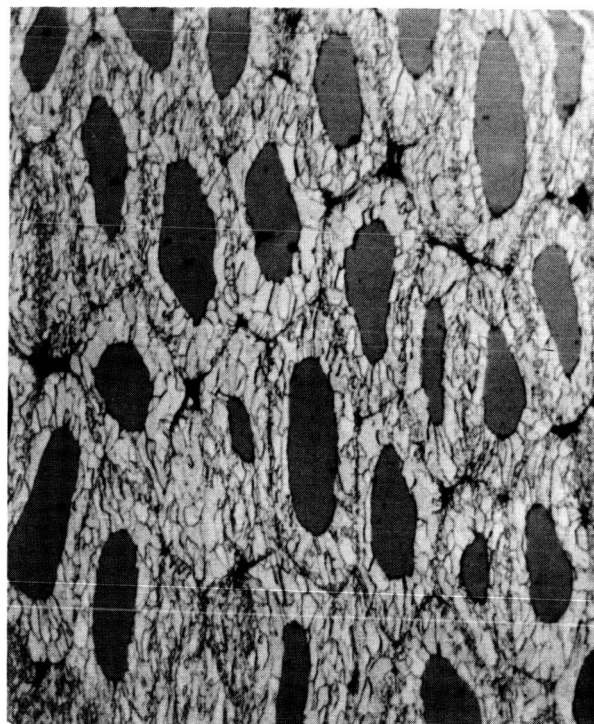


(d) Rolled at 2050° C.

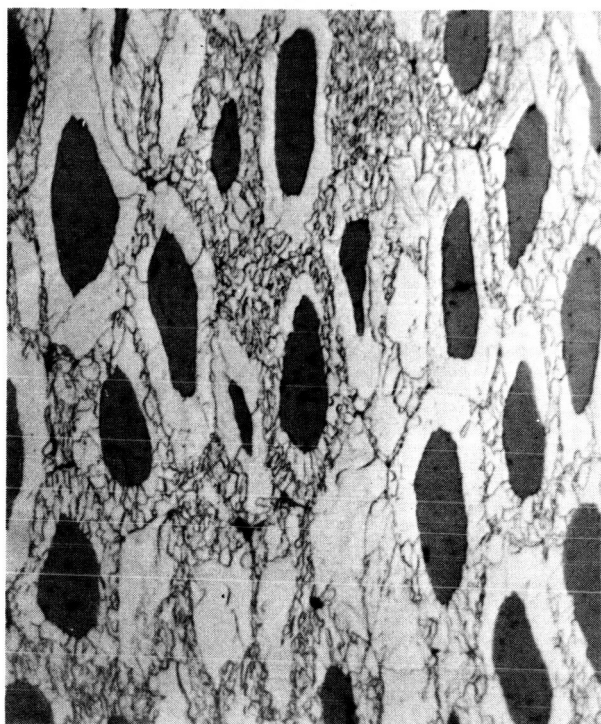
Figure 7. - Microstructures of tungsten - 20-volume-percent-UO₂ cermet rolled at various temperatures. Can assemblies rolled 50 percent. Unetched; X100.



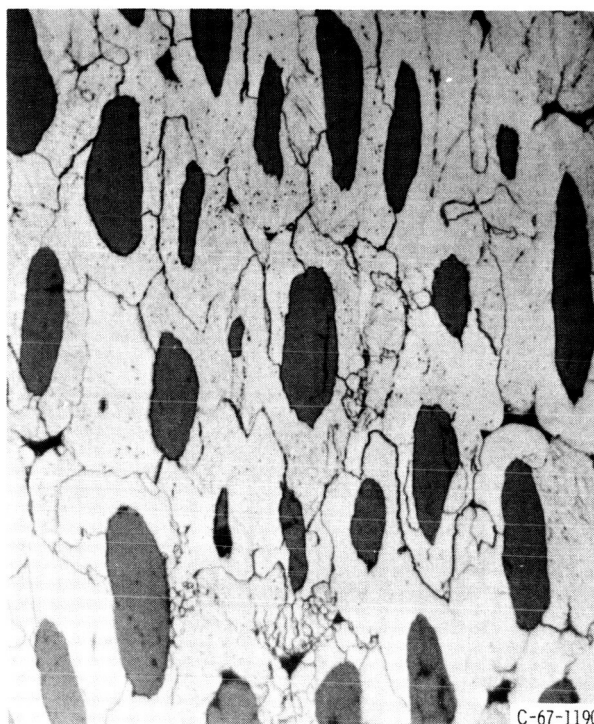
(a) Rolled at 1200° C.



(b) Rolled at 1450° C.



(c) Rolled at 1750° C.



(d) Rolled at 2050° C.

Figure 8. - Microstructures of tungsten - 20-volume-percent-UO₂ cermets rolled at various temperatures. Can assemblies rolled 50 percent. Murakami's reagent; X250.

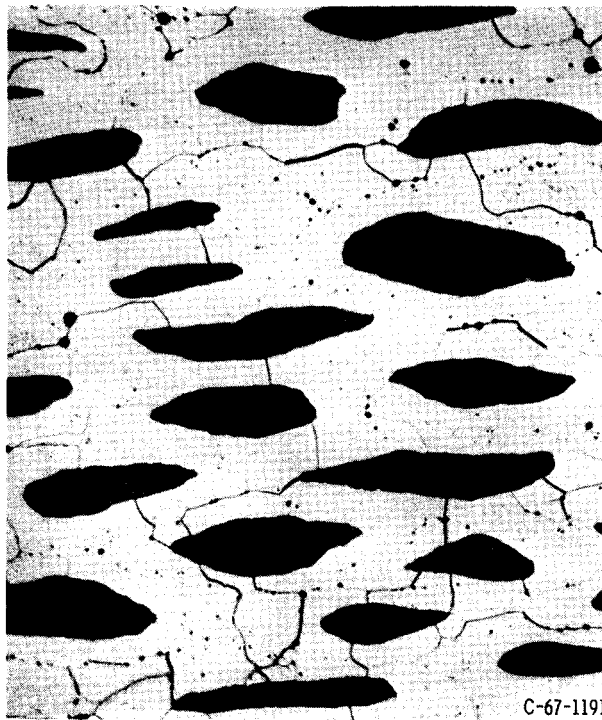


Figure 9. - Microstructure of tungsten - 20-volume-percent- UO_2 cermet rolled 50 percent at 1750°C and then heated to 2500°C for 2 hours in hydrogen to remove duplex grain structure. Murakami's reagent; X250.

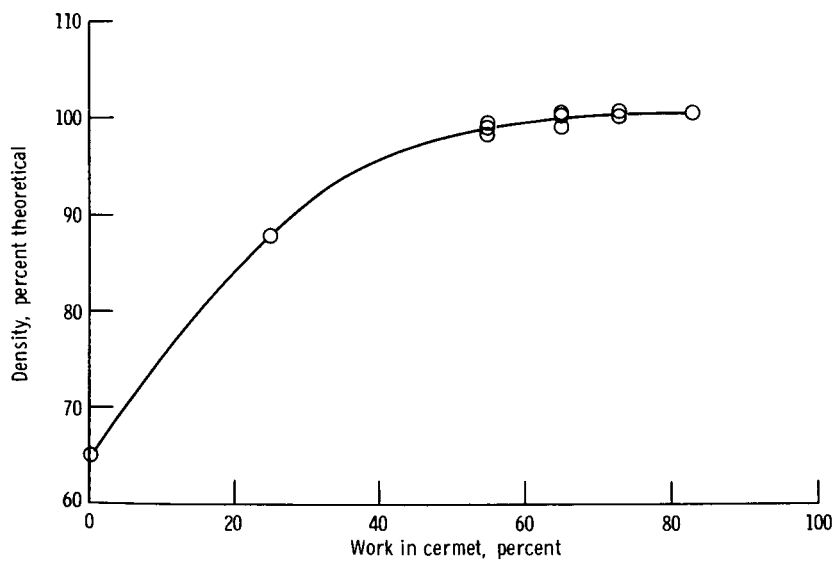
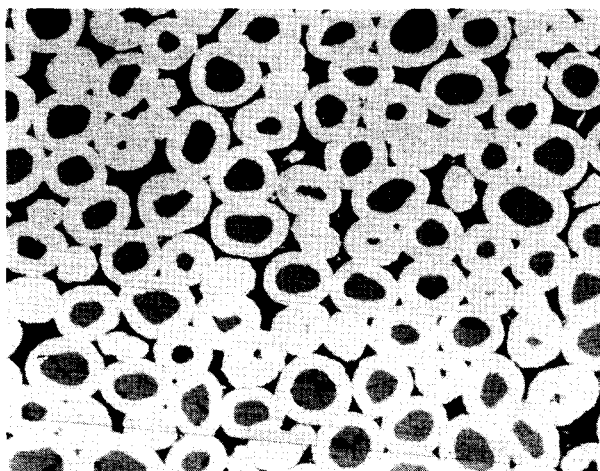
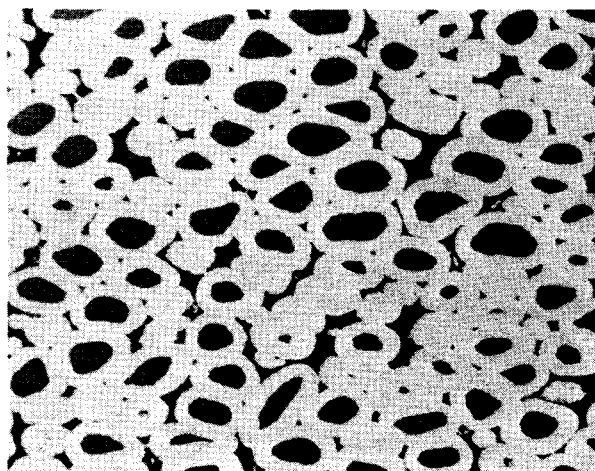


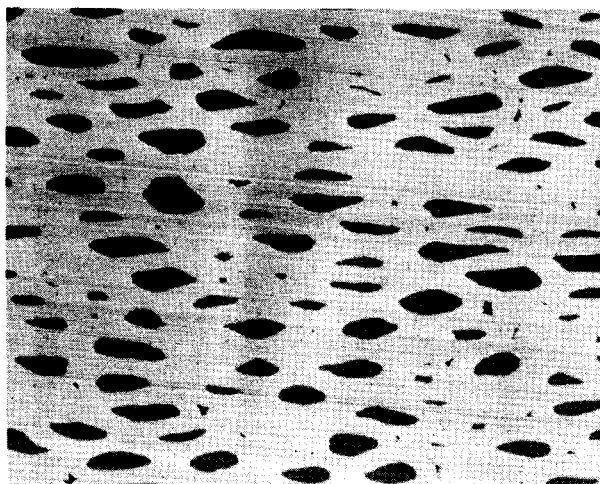
Figure 10. - Effect of hot working on density of tungsten - 20-volume-percent- UO_2 plates consolidated from tungsten-coated UO_2 particles. Rolling temperature, 1700°C .



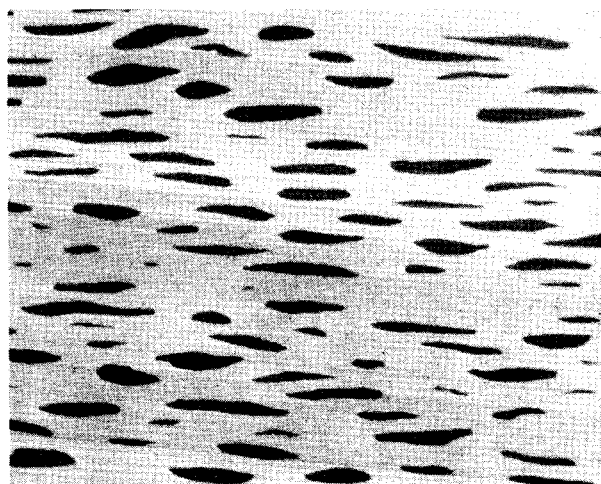
(a) Worked 25 percent.



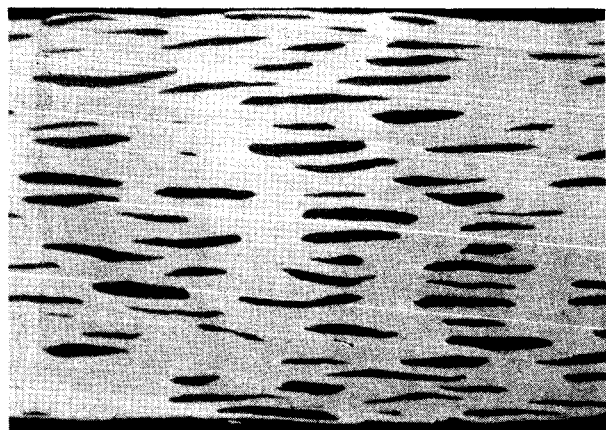
(b) Worked 46 percent.



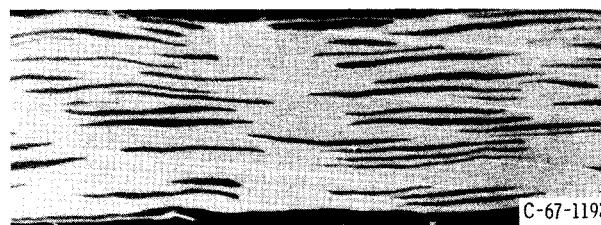
(c) Worked 55 percent.



(d) Worked 65 percent.



(e) Worked 72 percent.



(f) Worked 85 percent.

Figure 11. - Microstructures of tungsten - 20-volume-percent- UO_2 cermets rolled various amounts at 1700°C . Unetched; X100.

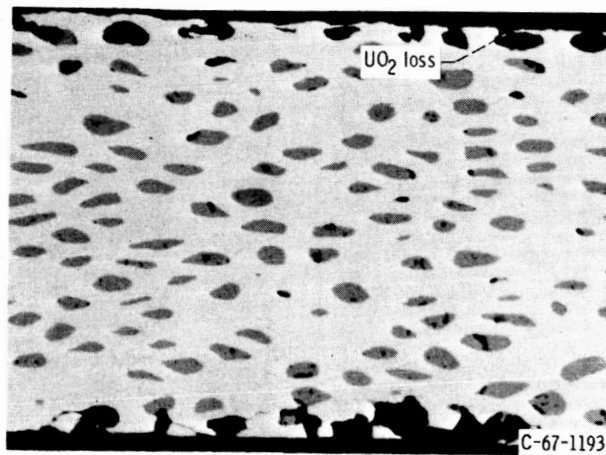
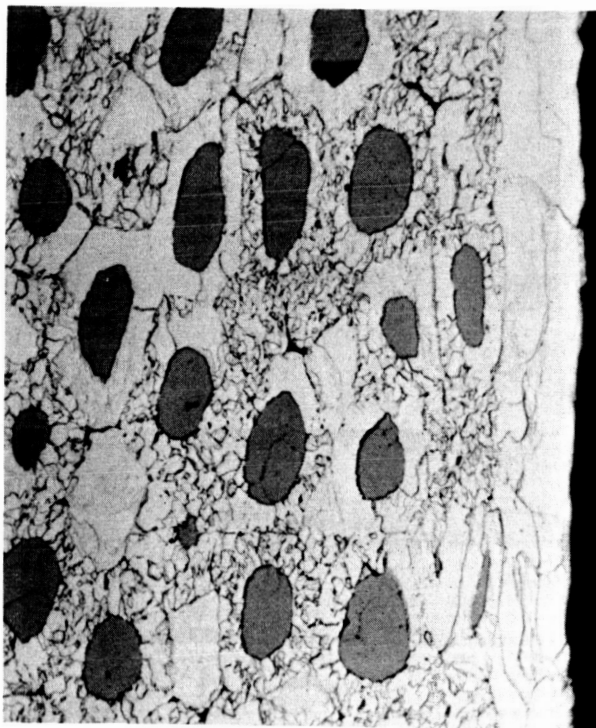
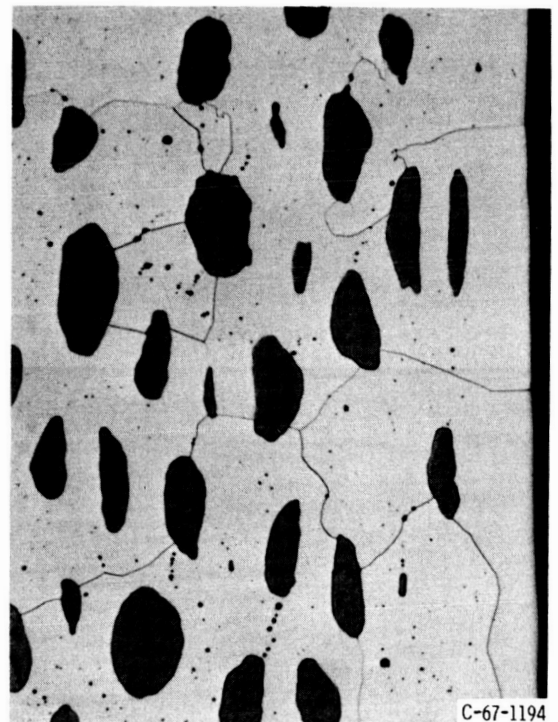


Figure 12. - Transverse section of roll compacted tungsten - 20-volume-percent- UO_2 cermet reduced 50 percent in thickness in the decanned condition. Sample lost 11 percent of UO_2 after 10 hours at 2500°C in flowing hydrogen. Unetched; X100.

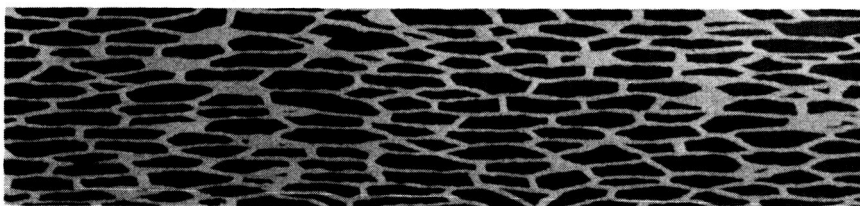


(a) As rolled.

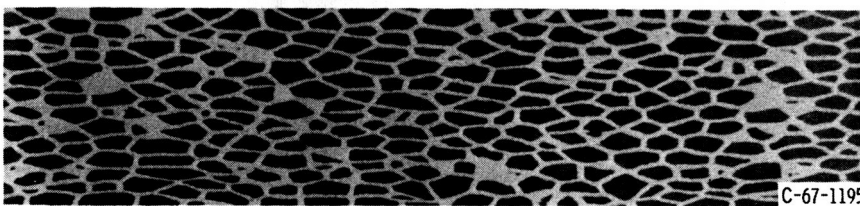


(b) Heated to 2500°C for 2 hours.

Figure 13. - Transverse section of roll compacted tungsten- UO_2 cermet showing core-cladding interface. Cladding applied during rolling in the canned condition. Murakami's reagent; X250.



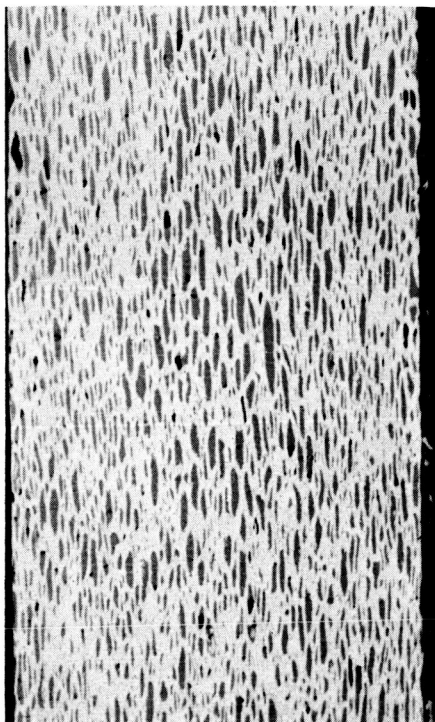
(a) Longitudinal section.



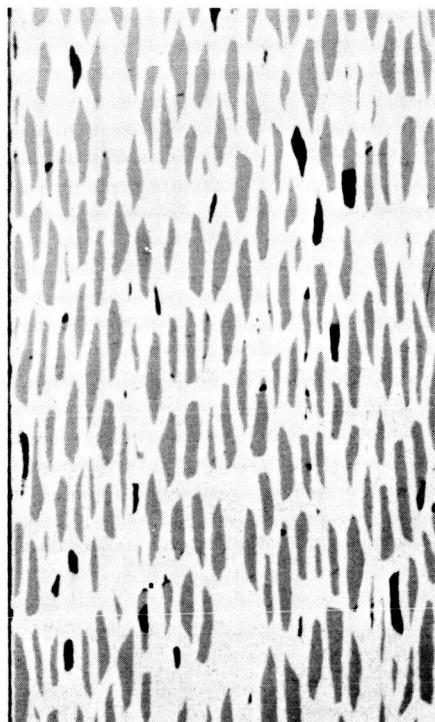
(b) Transverse section.

Figure 14. - Thin (0.010 in. (0.025 cm)) tungsten - 60-volume-percent-UO₂ cermet produced by roll compaction of coated particles. Unetched; X100.

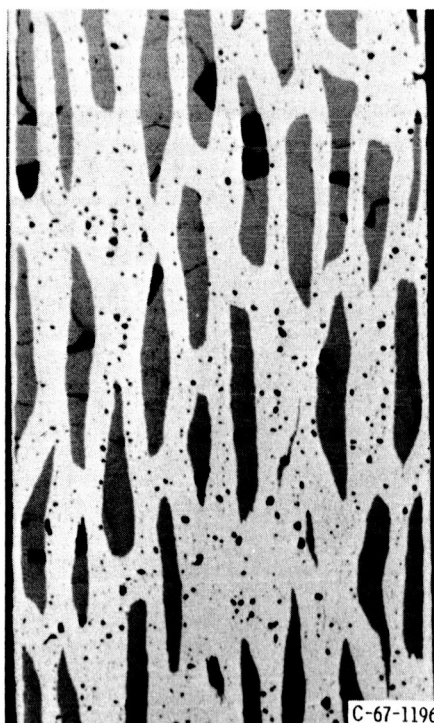
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(a) 10- to 30-micron UO_2 particles.



(b) 30- to 70-micron UO_2 particles.



(c) 70- to 130-micron UO_2 particles.

Figure 15. - Roll compacted tungsten - 35-volume-percent- UO_2 cermets fabricated from tungsten-coated UO_2 particles of various sizes. Unetched; X100.

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